

## Supporting Information

*for*

### Transition metal-free assembly of 1,3,5-triazines by using ethyl bromodifluoroacetate as C1 source

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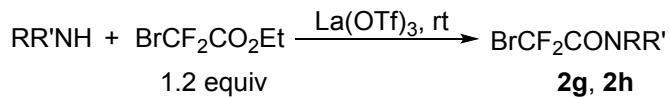
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## **1. General Considerations**

All chemicals were purchased from Adamas Reagent, energy chemical company, J&K, Scientific Ltd, Bide Pharmatech Ltd and Tansoole. The solvents were purchased from commercial suppliers and used without further purification. Unless stated otherwise, reactions were conducted in an over-dried schlenk tube with volume of 25 ml under N<sub>2</sub> atmosphere at 110°C. Flash column chromatography was performed over silica gel (200-300 mesh). <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz <sup>1</sup>H, 125 MHz <sup>13</sup>C) at room temperature. Chemical shifts were reported in ppm on the scale relative to CDCl<sub>3</sub> ( $\delta$  = 7.26 for <sup>1</sup>H-NMR ,  $\delta$  = 77.00 for <sup>13</sup>C-NMR) as an internal reference. Coupling constants (J) were reported in Hertz (Hz). The following abbreviations are used to indicate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. High resolution mass spectra were recorded using a Thermo Fisher Scientific LTQ FT Ultra or Waters Micromass GCT Premier instrument.

## 2. Experimental Procedures

### General procedure for the synthesis of bromodifluoroacetamides (**2g**, **2h**)



To a round-bottom flask equipped with stir bar was added amine (5 mmol) under argon, then ethyl bromodifluoroacetate (1.2 equiv) was added with lanthanum trifluoromethanesulfonate (5 mol%). The mixture was stirred at the room temperature and monitored by TLC. After the amine was exhausted, the mixture was extracted with AcOEt, and then the extract was washed with brine and dried over MgSO<sub>4</sub>. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel to give the corresponding amide **2**.

### General procedure for the amidines for the synthesis of symmetrical 2,4-disubstituted-1,3,5-triazines

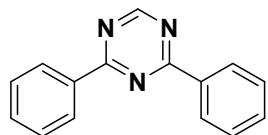
Amidines **1** (0.4 mmol), Na<sub>2</sub>CO<sub>3</sub> (169.6 mg, 4.0 equiv) were sequentially added to a 25 mL schlenk tube with agitated magnetons, followed by addition of BrCF<sub>2</sub>CO<sub>2</sub>Et (2.25 equiv) was added in acetonitrile (2.5 mL) with a nitrogen atmosphere. The mixture was stirred at 110°C for 12 h. The solution was then cooled to r.t. The reaction was monitored by TLC analysis. After the reaction was completed, the resulting mixture was evaporated to dryness and the crude product was purified with flash chromatography (silica gel, ethyl acetate: petroleum ether: = 1:50 ~ 1:100) to afford the desired symmetrical 2,4-disubstituted-1,3,5-triazines.

### General procedure for the two different amidines for the synthesis of unsymmetrical 2,4-disubstituted-1,3,5-triazine

Amidines **1** (0.3 mmol), amidines **1'** (0.6 mmol), Na<sub>2</sub>CO<sub>3</sub> (169.6 mg, 4.0 equiv) were sequentially added to a 25 mL schlenk tube with agitated magnetons, followed by addition of BrCF<sub>2</sub>CO<sub>2</sub>Et (2.25 equiv) was added in acetonitrile (2.5 mL) with a nitrogen atmosphere. The mixture was stirred at 110°C for 12 h. The solution was then cooled to r.t. The reaction was monitored by TLC analysis. After the reaction was completed, the resulting mixture was evaporated under vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate: petroleum ether: = 1:50 ~ 1:100) to afford the desired unsymmetrical 2,4-disubstituted-1,3,5-triazines.

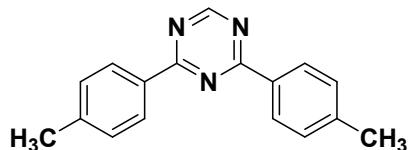
### 3. Characterization of Products

#### 2,4-diphenyl-1,3,5-triazine (3a)



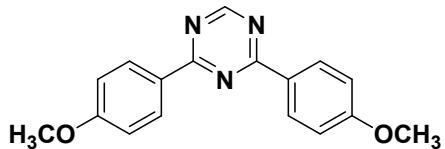
white solid, 40.1 mg, 86% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.26 (s, 1H), 8.66 – 8.64 (m, 4H), 7.63 – 7.60 (m, 2H), 7.58 – 7.54 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.4, 166.8, 135.6, 132.8, 128.9, 128.8. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> Calcd for  $\text{C}_{15}\text{H}_{12}\text{N}_3^+$ , 234.1026; Found: 234.1021.

#### 2,4-di-p-tolyl-1,3,5-triazine (3b)



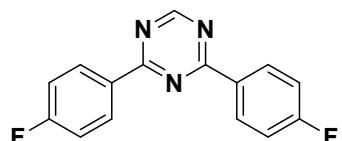
white solid, 41.8 mg, 80% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.19 (s, 1H), 8.52 (m,  $J = 8.2$  Hz, 4H), 7.34 (m,  $J = 8.0$  Hz, 4H), 2.46 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.2, 166.6, 143.4, 133.0, 129.5, 128.9, 21.7. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> Calcd for  $\text{C}_{17}\text{H}_{16}\text{N}_3^+$ , 262.1339; Found: 262.1336.

#### 2,4-bis(4-methoxyphenyl)-1,3,5-triazine (3c)



white solid, 44.5 mg, 76% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.10 (s, 1H), 8.78 – 8.31 (m, 4H), 7.14 – 6.77 (m, 4H), 3.89 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 166.3, 163.4, 130.8, 128.2, 114.0, 55.5. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> Calcd for  $\text{C}_{17}\text{H}_{16}\text{N}_3\text{O}_2^+$ , 294.1237; Found: 294.1240.

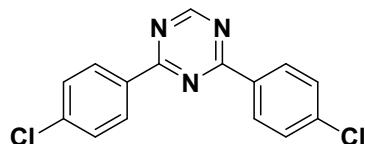
#### 2,4-bis(4-fluorophenyl)-1,3,5-triazine (3d)



white solid, 44.7 mg, 83% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.19 (s, 1H), 8.88 –

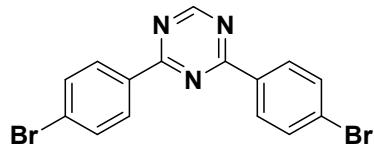
8.38 (m, 4H), 7.25 – 7.18 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.3, 166.7, 166.0 (d,  $J = 252.5$  Hz), 131.6 (d,  $J = 2.5$  Hz), 131.3 (d,  $J = 8.8$  Hz), 115.9 (d,  $J = 22.5$  Hz).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -106.3. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{10}\text{F}_2\text{N}_3^+$ , 270.0837; Found: 270.0836.

### 2,4-bis(4-chlorophenyl)-1,3,5-triazine (3e)



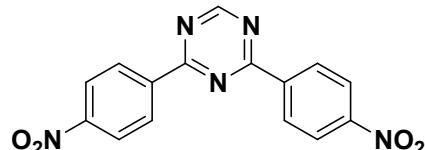
white solid, 35.0 mg, 58% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.23 (s, 1H), 8.92 – 8.24 (m, 4H), 7.87 – 7.33 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 166.8, 139.4, 133.9, 130.2, 129.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{N}_3^+$ , 302.0246; Found: 302.0245.

### 2,4-bis(4-nitrophenyl)-1,3,5-triazine (3f)



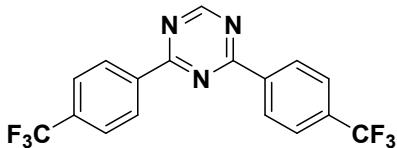
white solid, 36.7 mg, 60% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.23 (s, 1H), 8.48 (m,  $J = 8.4$  Hz, 4H), 7.85 – 7.54 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.7, 166.9, 134.3, 132.1, 130.4, 128.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{10}\text{Br}_2\text{N}_3^+$ , 389.9236; Found: 389.9236.

### 2,4-bis(4-nitrophenyl)-1,3,5-triazine (3g)



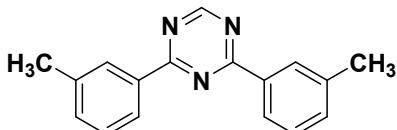
light yellow solid, 19.4 mg, 30% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.69 – 9.37 (m, 1H), 8.93 – 8.78 (m, 4H), 8.48 – 8.40 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 167.4, 150.8, 140.6, 130.0, 124.0. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{15}\text{H}_{10}\text{N}_5\text{O}_4^+$ , 346.0547; Found: 346.0542.

### **2,4-bis(4-(trifluoromethyl)phenyl)-1,3,5-triazine (3h)**



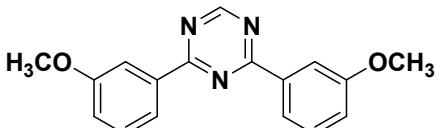
white solid, 41.3 mg, 56% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.35 (s, 1H), 8.76 (d,  $J = 8.1$  Hz, 4H), 7.82 (d,  $J = 8.2$  Hz, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 167.1, 138.5, 134.4 (q,  $J = 31.3$  Hz), 129.3, 125.8 (q,  $J = 3.8$  Hz), 123.8 (d,  $J = 271.3$  Hz).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.0. HRMS (ESI)  $m/z$ : [M+H] $^+$  Calcd for  $\text{C}_{17}\text{H}_{10}\text{F}_6\text{N}_3^+$ , 370.0773; Found: 370.0774.

### **2,4-di-m-tolyl-1,3,5-triazine (3i)**



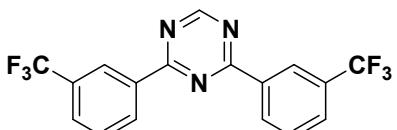
white solid, 40.2 mg, 77% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.21 (s, 1H), 8.44 – 8.41 (m, 4H), 7.45 – 7.38 (m, 4H), 2.47 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.5, 166.6, 138.5, 135.6, 133.6, 129.4, 128.7, 126.2, 21.5. HRMS (ESI)  $m/z$ : [M+H] $^+$  Calcd for  $\text{C}_{17}\text{H}_{16}\text{N}_3^+$ , 216.1339; Found: 216.1340.

### **2,4-bis(3-methoxyphenyl)-1,3,5-triazine (3j)**



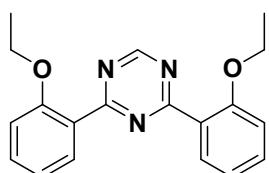
white solid, 41.0 mg, 70% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.24 (s, 1H), 8.24 (m,  $J = 7.7$  Hz, 2H), 8.19 – 8.14 (m, 2H), 7.45 (m,  $J = 7.9$  Hz, 2H), 7.15 (m,  $J = 7.9, 2.4$  Hz, 2H), 3.93 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.1, 166.7, 160.0, 136.9, 129.8, 121.5, 119.2, 113.4, 55.5. HRMS (ESI)  $m/z$ : [M+H] $^+$  Calcd for  $\text{C}_{17}\text{H}_{16}\text{N}_3\text{O}_2^+$ , 294.1237; Found: 294.1239.

### **2,4-bis(4-(trifluoromethyl)phenyl)-1,3,5-triazine (3k)**



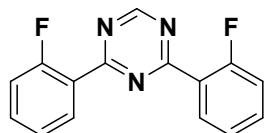
white solid, 47.2 mg, 64% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.41 (s, 1H), 8.37 (m,  $J = 7.8, 1.8$  Hz, 2H), 7.67 – 7.50 (m, 2H), 7.34 (m,  $J = 7.8, 1.0$  Hz, 2H), 7.31 – 7.21 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.4, 167.1, 136.1, 132.1, 131.5 (q,  $J = 32.5$  Hz), 129.5 (q,  $J = 2.5$  Hz), 129.5, 125.8 (q,  $J = 3.8$  Hz), 123.9 (d,  $J = 270.0$  Hz).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.7. HRMS (ESI)  $m/z$ : [M+H] $^+$  Calcd for  $\text{C}_{17}\text{H}_{10}\text{F}_6\text{N}_3^+$ , 370.0773; Found: 370.0773.

### 2,4-bis(2-ethoxyphenyl)-1,3,5-triazine (3l)



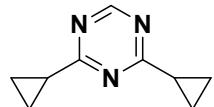
light yellow solid, 41.7 mg, 65% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.31 (s, 1H), 8.00 – 7.96 (m, 2H), 7.48 – 7.44 (m, 2H), 7.09 – 7.03 (m, 4H), 4.17 (q,  $J = 7.0$  Hz, 4H), 1.44 (t,  $J = 7.0$  Hz, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 165.6, 158.1, 132.6, 132.3, 126.4, 120.6, 113.6, 64.7, 14.8. HRMS (ESI)  $m/z$ : [M+H] $^+$  Calcd for  $\text{C}_{19}\text{H}_{20}\text{N}_3\text{O}_2^+$ , 322.1550; Found: 322.1551.

### 2,4-bis(2-fluorophenyl)-1,3,5-triazine (3m)



white solid, 42.0 mg, 78% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.33 (s, 1H), 8.90 (s, 2H), 8.87 – 8.82 (m, 2H), 7.91 – 7.86 (m, 2H), 7.74 – 7.69 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.4 (d,  $J = 5.0$  Hz), 166.56, 162.3 (d,  $J = 258.7$  Hz), 134.0 (d,  $J = 8.8$  Hz), 132.2, 124.4 (d,  $J = 3.8$  Hz), 124.0 (d,  $J = 7.5$  Hz), 117.3 (d,  $J = 22.5$  Hz).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.2. HRMS (ESI)  $m/z$ : [M+H] $^+$  Calcd for  $\text{C}_{15}\text{H}_{10}\text{F}_2\text{N}_3^+$ , 270.0837; Found: 270.0840.

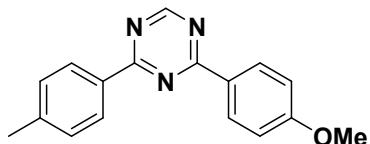
### 2,4-dicyclopropyl-1,3,5-triazine (3n)



light yellow liquid, 17.1 mg, 53% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.69 (s, 1H), 2.09 – 2.04 (m, 2H), 1.21 – 1.18 (m, 4H), 1.13 – 1.09 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,

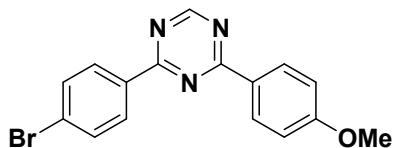
$\text{CDCl}_3$ )  $\delta$  179.6, 164.7, 17.8, 11.9. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> Calcd for  $\text{C}_9\text{H}_{12}\text{N}_3^+$ , 162.1026; Found: 162.1028.

### 2-(4-methoxyphenyl)-4-(p-tolyl)-1,3,5-triazine (3bc)



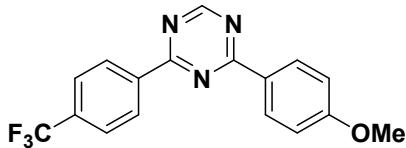
white solid, 42.4 mg, 51% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.15 (s, 1H), 8.61 – 8.57 (m, 2H), 8.52 – 8.49 (m, 2H), 7.36 – 7.32 (m, 2H), 7.06 – 7.02 (m, 2H), 3.91 (s, 3H), 2.46 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.1, 170.8, 166.5, 163.5, 143.3, 133.1, 130.8, 129.5, 128.8, 128.2, 114.1, 55.5, 21.7. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> Calcd for  $\text{C}_{17}\text{H}_{16}\text{N}_3\text{O}^+$ , 278.1288; Found: 278.1291.

### 2-(4-bromophenyl)-4-(4-methoxyphenyl)-1,3,5-triazine (3cf)



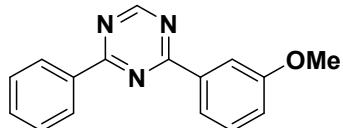
white solid, 51.2 mg, 50% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.16 (s, 1H), 8.59 – 8.56 (m, 2H), 8.49 – 8.46 (m, 2H), 7.68 – 7.65 (m, 2H), 7.05 – 7.02 (m, 2H), 3.91 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.0, 170.3, 166.6, 163.7, 134.7, 132.0, 130.9, 130.3, 127.8, 127.7, 114.1, 55.5. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> Calcd for  $\text{C}_{16}\text{H}_{13}\text{BrN}_3\text{O}^+$ , 342.0237; Found: 342.0236.

### 2-(4-methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-1,3,5-triazine (3cg)



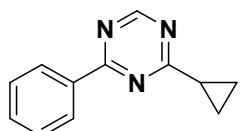
white solid, 45.7 mg, 46% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.22 (s, 1H), 8.74 – 8.71 (m, 2H), 8.62 – 8.58 (m, 2H), 7.82 – 7.78 (m, 2H), 7.06 – 7.03 (m, 2H), 3.92 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.2, 169.9, 166.8, 163.8, 139.1, 134.0 (q,  $J$  = 31.3 Hz), 131.0, 129.1, 127.7, 125.6 (q,  $J$  = 3.8 Hz), 123.9 (d,  $J$  = 271.3 Hz), 114.2, 55.5.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.9. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> Calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{N}_3\text{O}^+$ , 332.1005; Found: 332.1008.

### **2-(3-methoxyphenyl)-4-phenyl-1,3,5-triazine (3aj)**



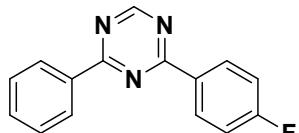
white solid, 35.5 mg, 45% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.25 (s, 1H), 8.65 – 8.62 (m, 2H), 8.28 – 8.23 (m, 1H), 8.20 – 8.16 (m, 1H), 7.63 – 7.59 (m, 1H), 7.57 – 7.53 (m, 2H), 7.48 – 7.44 (m, 1H), 7.17 – 7.13 (m, 1H), 3.94 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 171.2, 166.7, 160.0, 137.0, 135.5, 132.8, 129.8, 128.9, 128.8, 121.5, 119.2, 113.4, 55.5. HRMS (ESI)  $m/z$ : [M+H] $^+$  Calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_3\text{O}^+$ , 264.1131; Found: 264.1135.

### **2-cyclopropyl-4-phenyl-1,3,5-triazine (3an)**



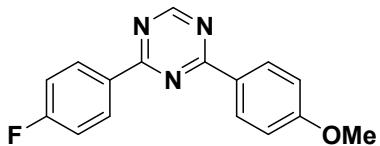
Light yellow liquid, 17.8 mg, 30% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.98 (s, 1H), 8.50 – 8.47 (m, 2H), 7.58 – 7.54 (m, 1H), 7.51 – 7.47 (m, 2H), 2.27 – 2.21 (m, 1H), 1.35 – 1.32 (m, 2H), 1.22 – 1.18 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  180.7, 170.4, 165.7, 135.5, 132.6, 128.8, 128.7, 18.2, 12.2. HRMS (ESI)  $m/z$ : [M+Na] $^+$  Calcd for  $\text{C}_{12}\text{H}_{11}\text{NaN}_3^+$ , 220.0845; Found: 220.0852.

### **2-(4-fluorophenyl)-4-phenyl-1,3,5-triazine (3ad)**



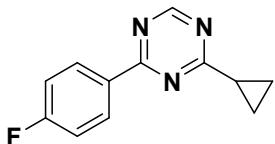
white solid, 59.5 mg, 79% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.21 (m,  $J = 16.0$  Hz, 1H), 8.67 – 8.59 (m, 4H), 7.57 (m,  $J = 8.3, 4.2$  Hz, 4H), 7.23 – 7.19 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 170.3, 166.0 (q,  $J = 252.5$  Hz), 166.7 (t,  $J = 3.8$  Hz), 135.6, 135.4, 132.9, 132.8, 131.7 (d,  $J = 2.5$  Hz), 131.6 (d,  $J = 2.5$  Hz), 131.3 (d,  $J = 8.8$  Hz), 128.8 (dd,  $J = 18.8$  Hz), 115.9 (d,  $J = 21.3$  Hz).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -106.2, -106.4. HRMS (ESI)  $m/z$ : [M+K] $^+$  Calcd for  $\text{C}_{15}\text{H}_{10}\text{FKN}_3^+$ , 290.0490; Found: 290.0494.

**2-(4-fluorophenyl)-4-(4-methoxyphenyl)-1,3,5-triazine (3dc)**



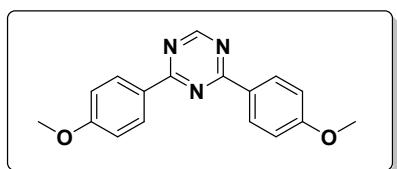
white solid, 43.8 mg, 52% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.16 (s, 1H), 8.66 – 8.62 (m, 2H), 8.60 – 8.57 (m, 2H), 7.21 (m,  $J = 8.7$  Hz, 2H), 7.06 – 7.02 (m, 2H), 3.92 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 170.1, 165.9 (d,  $J = 251.3$  Hz), 166.5, 163.6, 131.9 (d,  $J = 2.5$  Hz), 131.2 (d,  $J = 8.8$  Hz), 130.9, 127.9, 115.8 (d,  $J = 22.5$  Hz), 114.1, 55.5.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -106.8. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> Calcd for  $\text{C}_{16}\text{H}_{13}\text{FN}_3\text{O}^+$ , 282.1037; Found: 282.1036.

**2-cyclopropyl-4-(4-fluorophenyl)-1,3,5-triazine (3dn)**

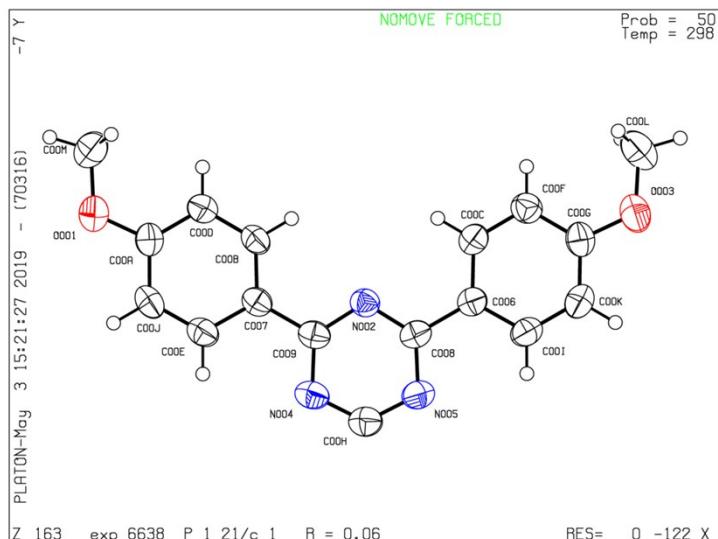


white solid, 25.5 mg, 40% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.95 (s, 1H), 8.52 – 8.48 (m, 2H), 7.19 – 7.14 (m, 2H), 2.26 – 2.18 (m, 1H), 1.34 – 1.31 (m, 2H), 1.23 – 1.19 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  180.8, 169.4, 165.8 (d,  $J = 251.3$  Hz), 165.7, 131.6 (d,  $J = 2.5$  Hz), 131.1 (d,  $J = 8.8$  Hz), 115.8 (d,  $J = 21.3$  Hz), 18.2, 12.3.  $^{19}\text{F}$  NMR (47 MHz,  $\text{CDCl}_3$ )  $\delta$  -106.8. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> Calcd for  $\text{C}_{12}\text{H}_{11}\text{FN}_3^+$ , 216.0932; Found: 216.0929.

#### 4. Crystal Structure of 3c



CCDC: 1913836



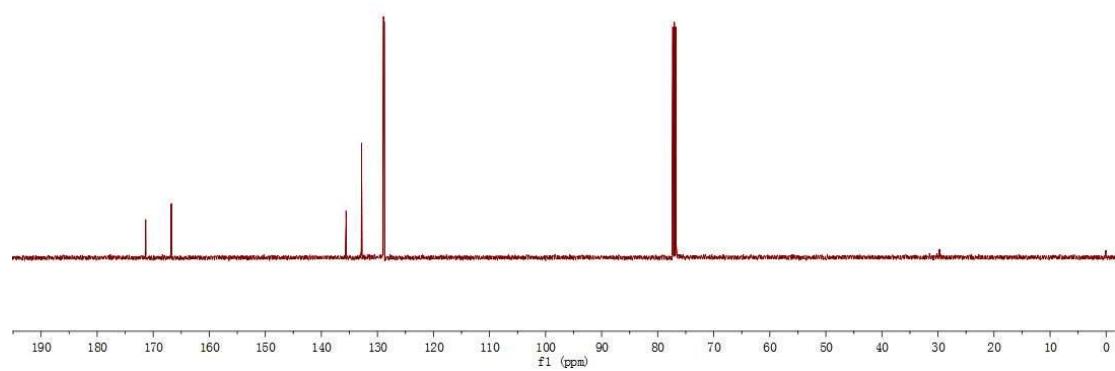
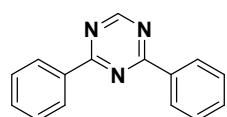
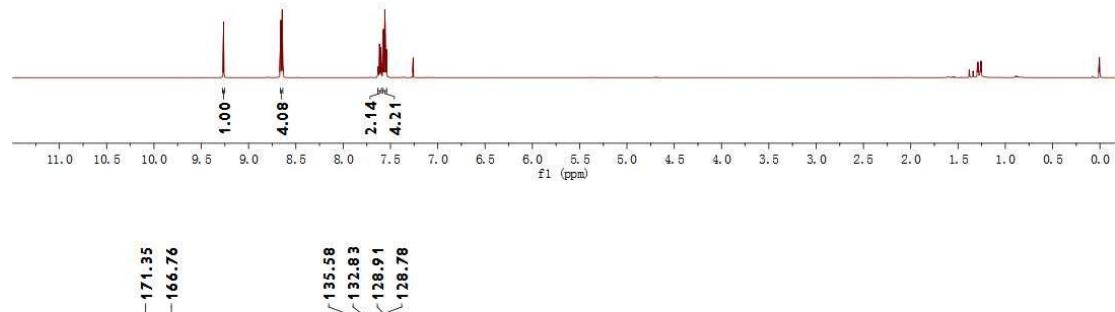
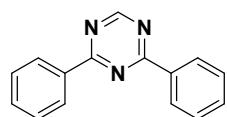
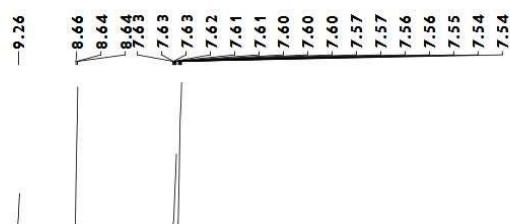
Bond precision:	C-C = 0.0035 Å	Wavelength=0.71073
Cell:	a=15.409(2)	b=8.2878(8)
	alpha=90	c=12.3822(16)
		beta=111.992(16)
Temperature:	298 K	gamma=90
	Calculated	Reported
Volume	1466.2(3)	1466.3(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C17 H14 N3 O2	0.67(C17 H14 N3 O2)
Sum formula	C17 H14 N3 O2	C11.333 H9.333 N2 O1.333
Mr	292.31	194.88
Dx,g cm <sup>-3</sup>	1.324	1.324
Z	4	6
Mu (mm <sup>-1</sup> )	0.089	0.089
F000	612.0	612.3
F000'	612.26	
h,k,lmax	18,9,14	18,9,14
Nref	2582	2576
Tmin,Tmax		0.741,1.000
Tmin'		
Correction method=	# Reported T Limits: Tmin=0.741 Tmax=1.000	
AbsCorr =	MULTI-SCAN	
Data completeness=	0.998	Theta(max)= 25.000
R(reflections)=	0.0630( 1717)	wR2(reflections)= 0.1828( 2576)

S = 1.077

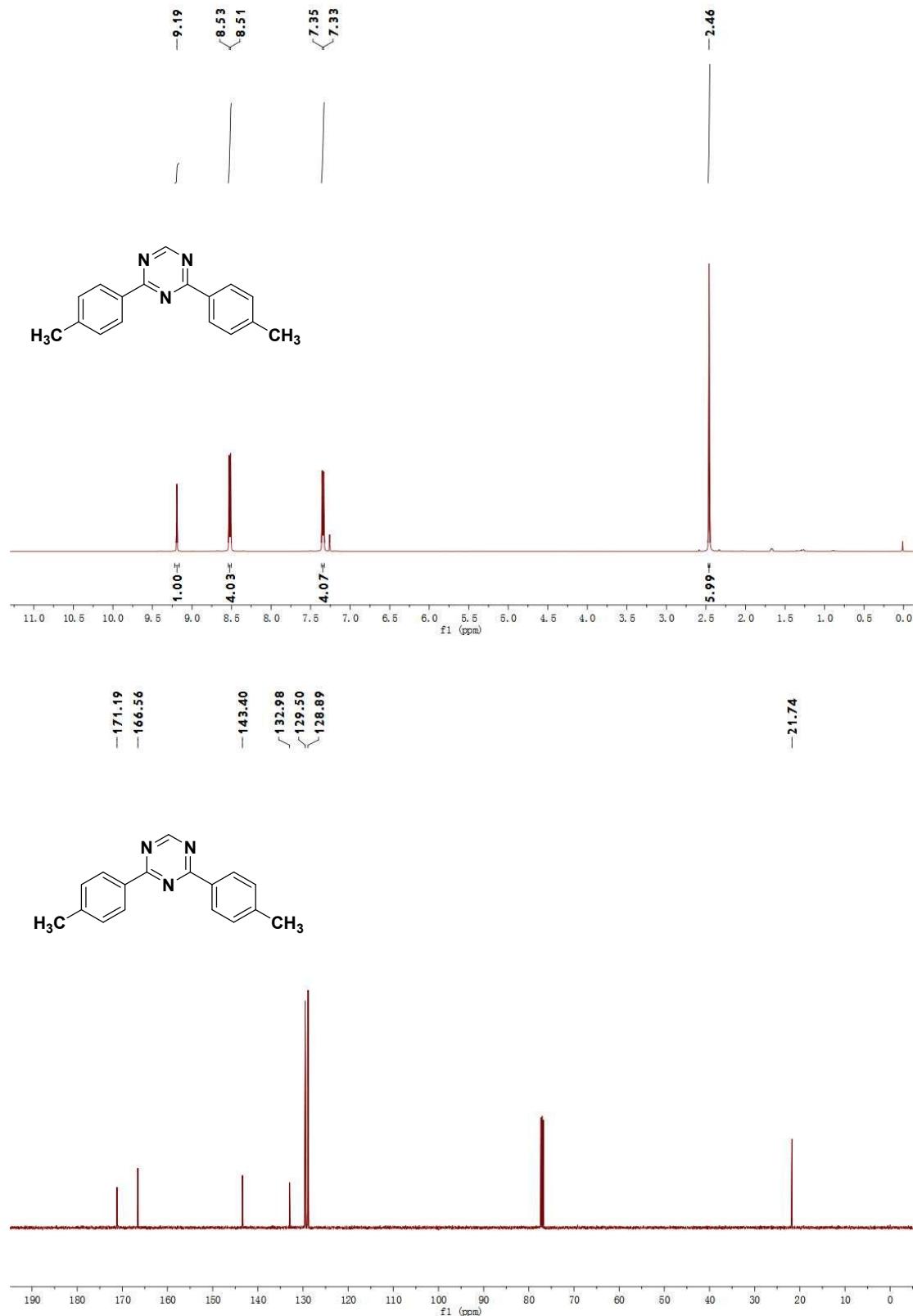
Npar= 200

## 5. NMR Spectra of Products

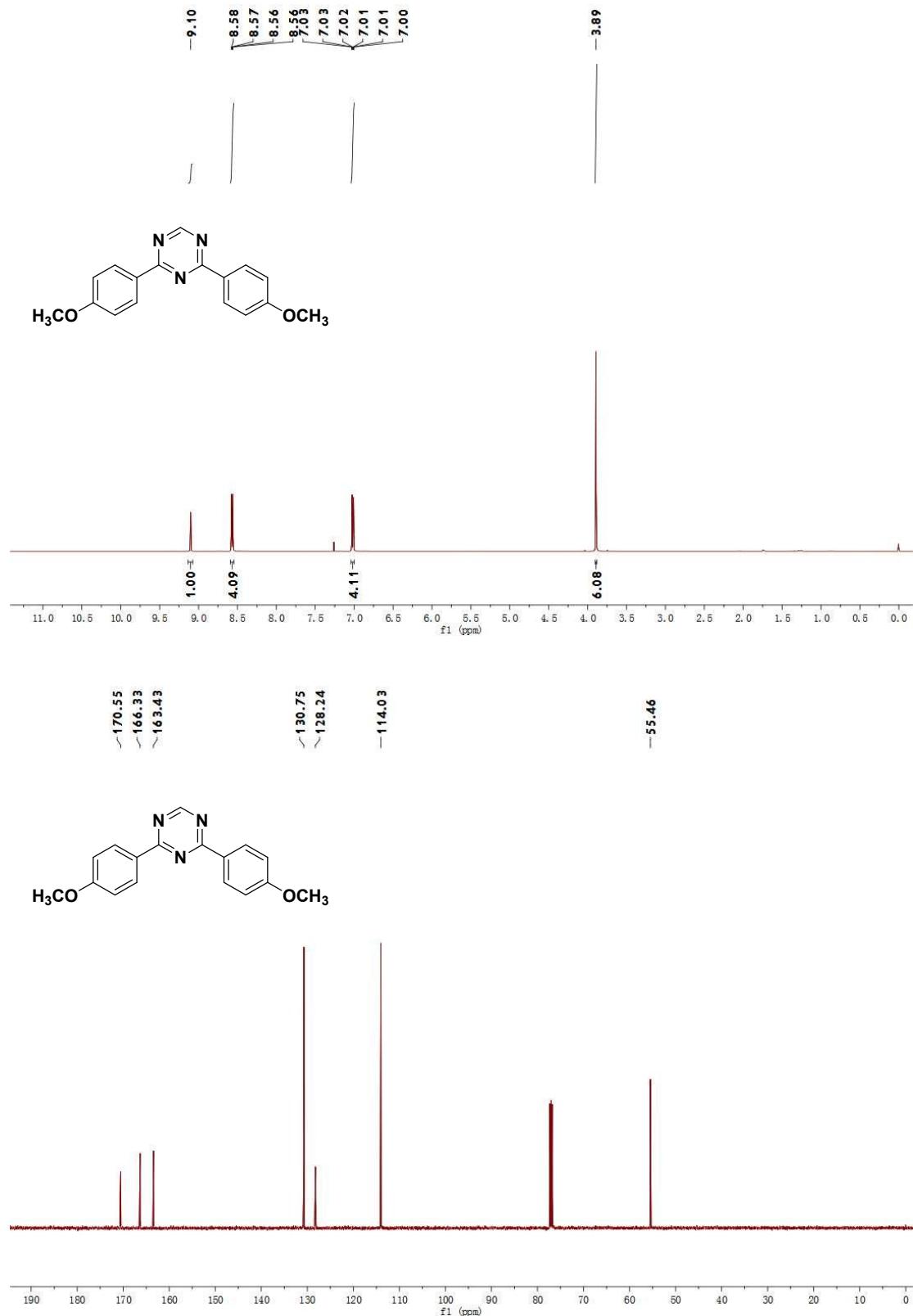
### 2,4-diphenyl-1,3,5-triazine (3a)



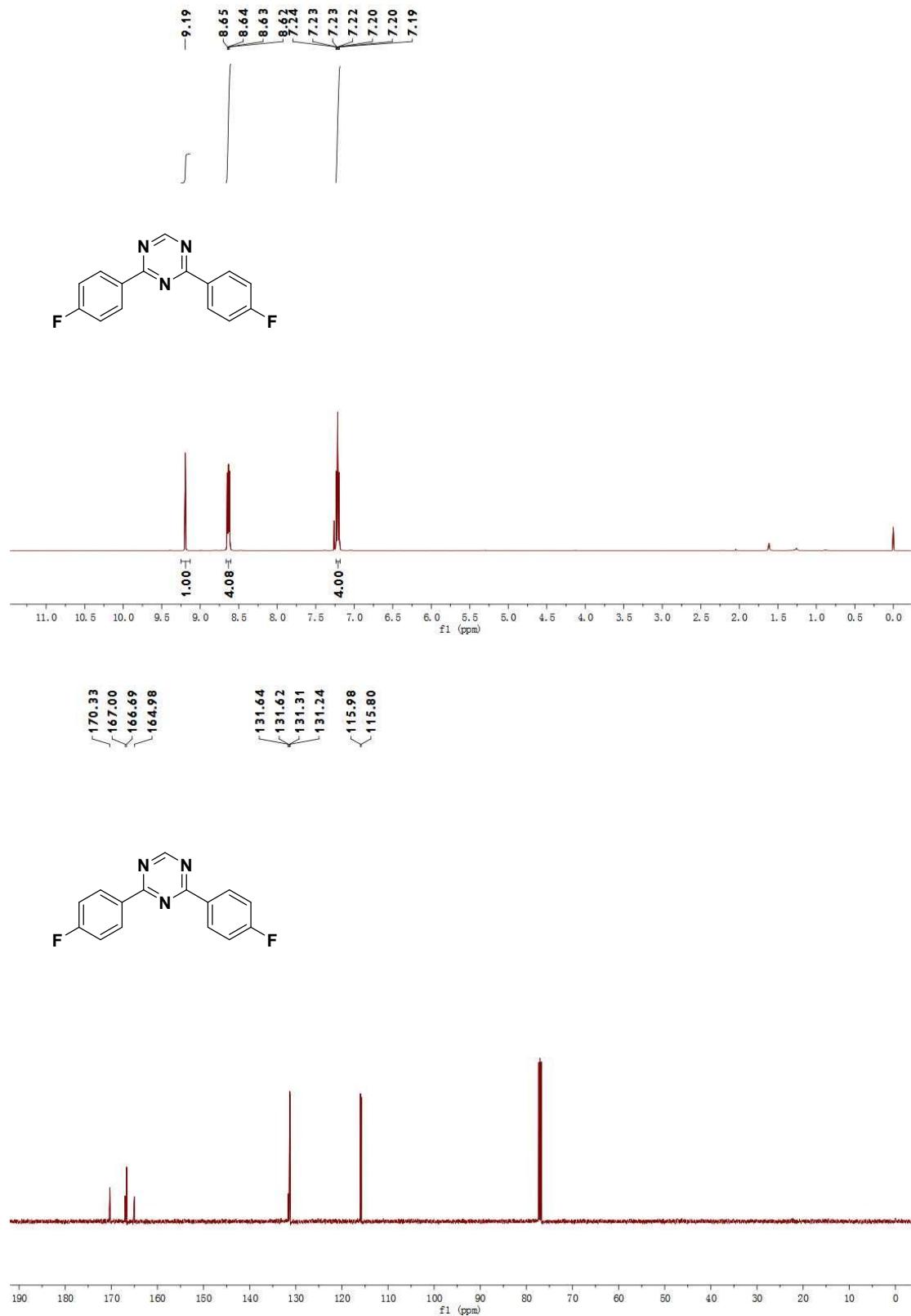
**2,4-di-p-tolyl-1,3,5-triazine (3b)**



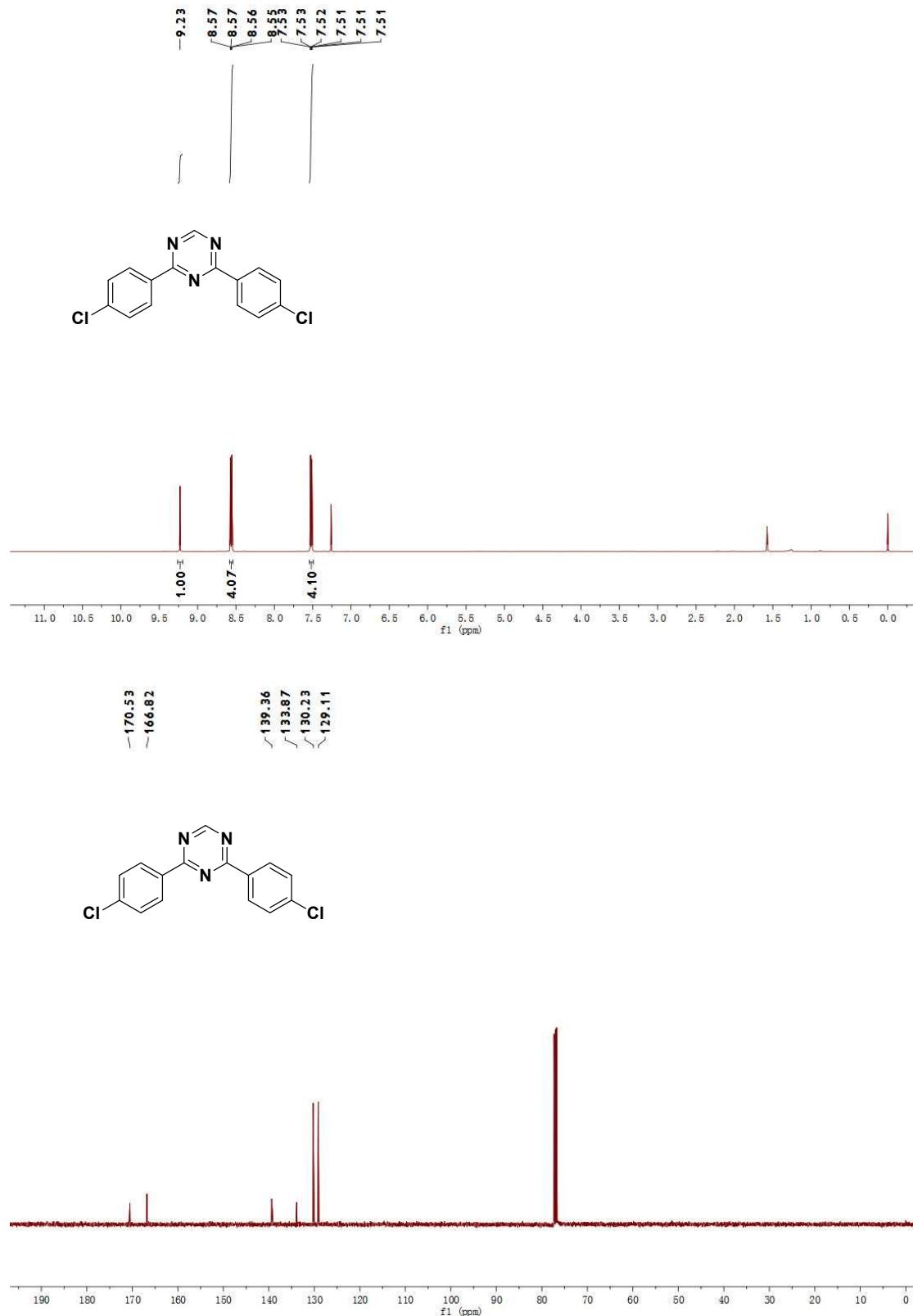
**2,4-bis(4-methoxyphenyl)-1,3,5-triazine (3c)**



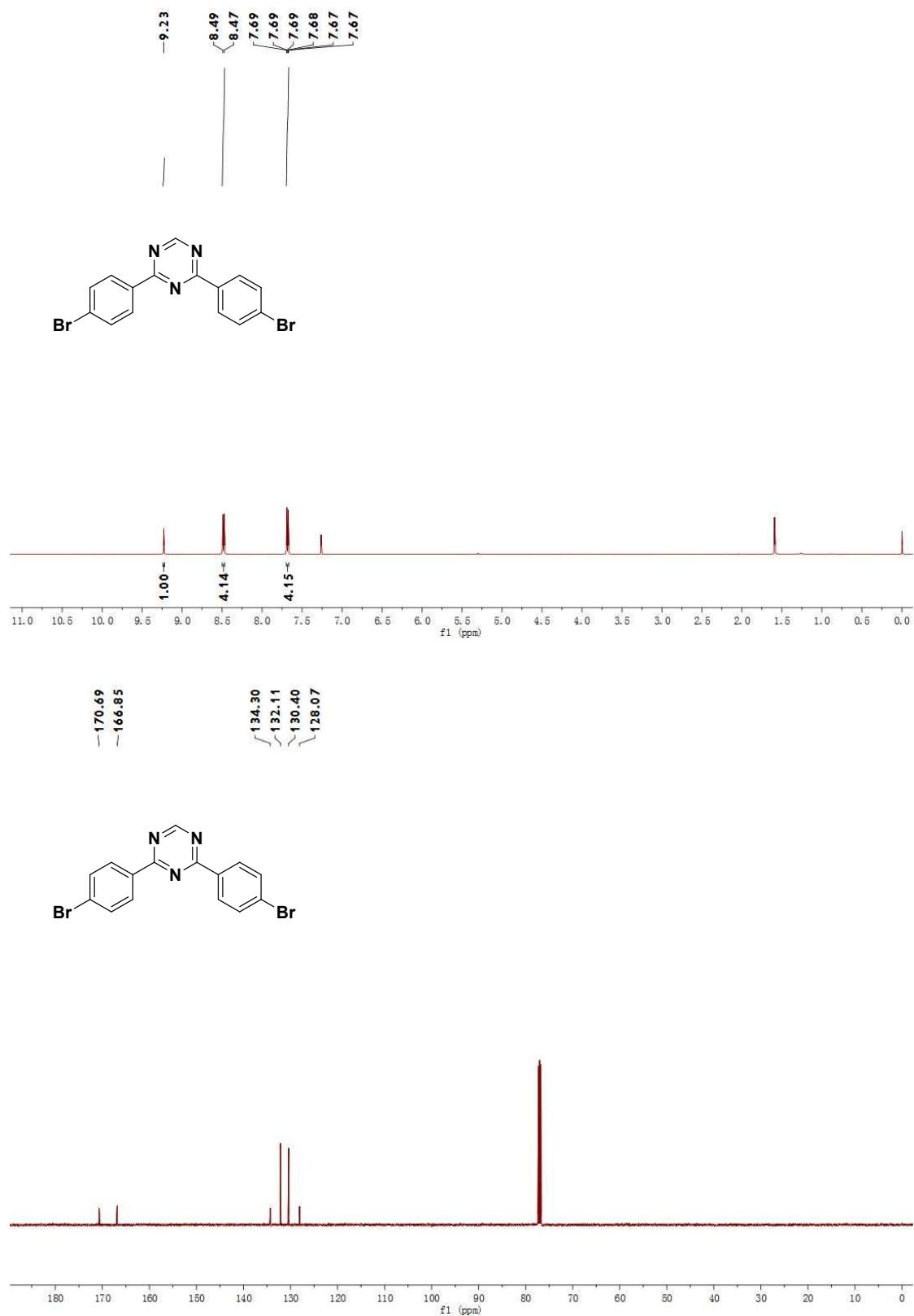
**2,4-bis(4-fluorophenyl)-1,3,5-triazine(3d)**



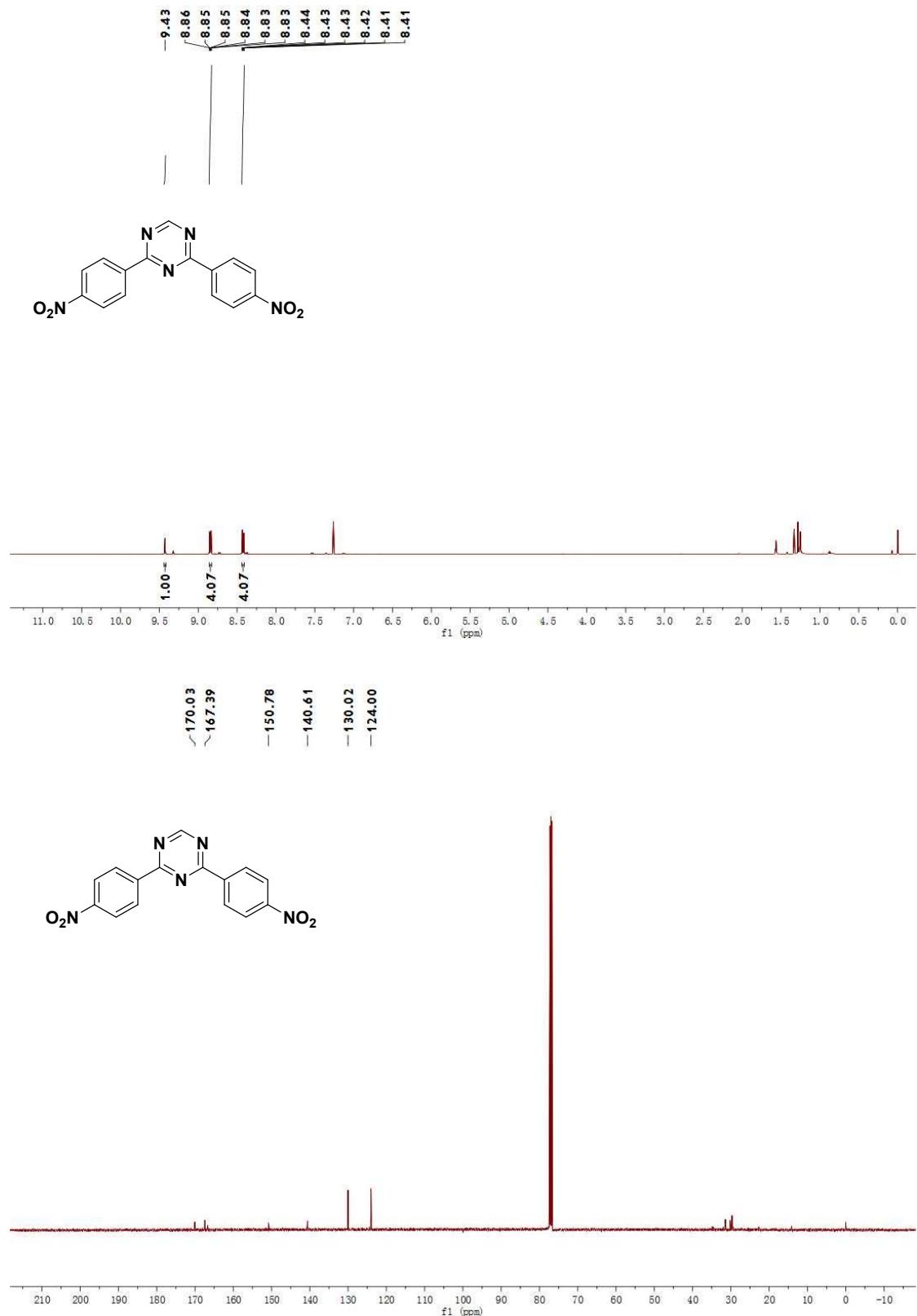
**2,4-bis(4-chlorophenyl)-1,3,5-triazine (3e)**



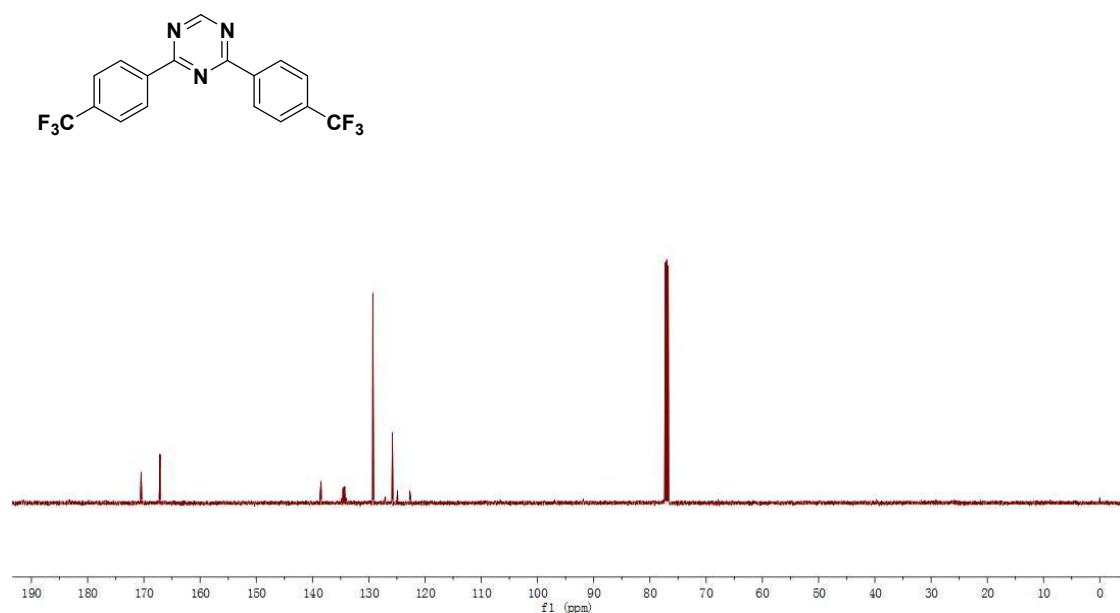
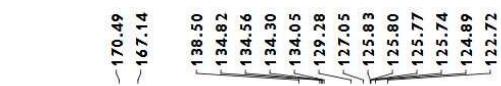
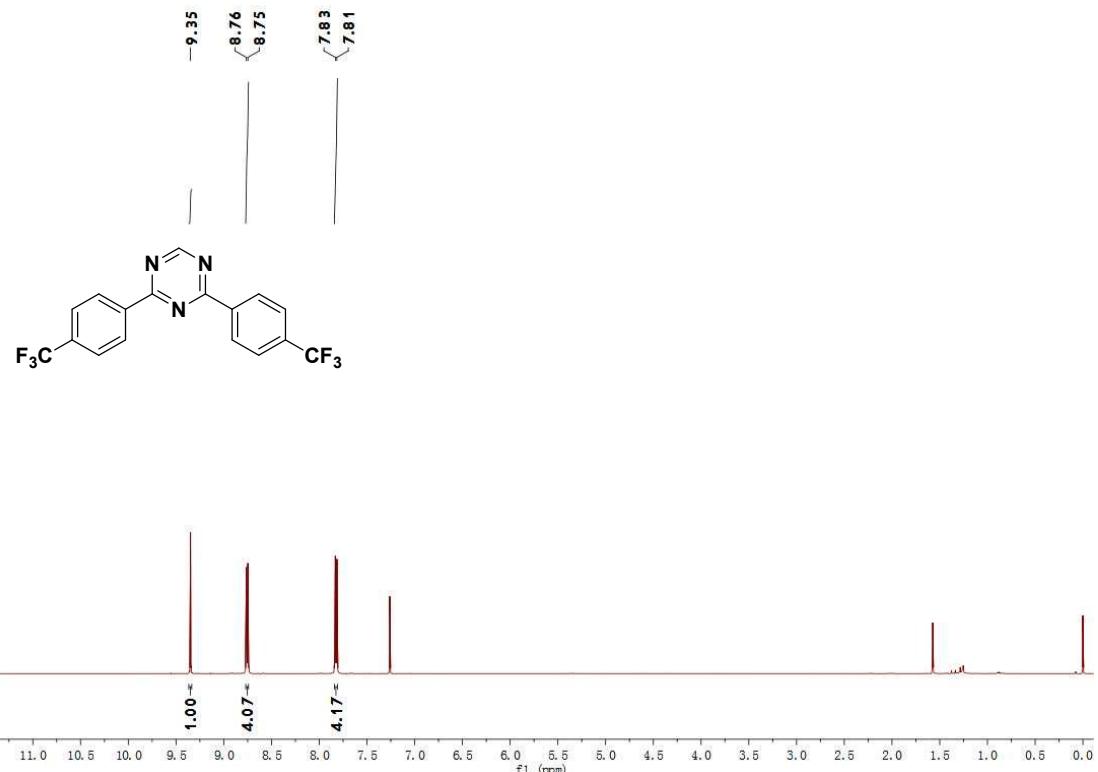
**2,4-bis(4-nitrophenyl)-1,3,5-triazine (3f)**



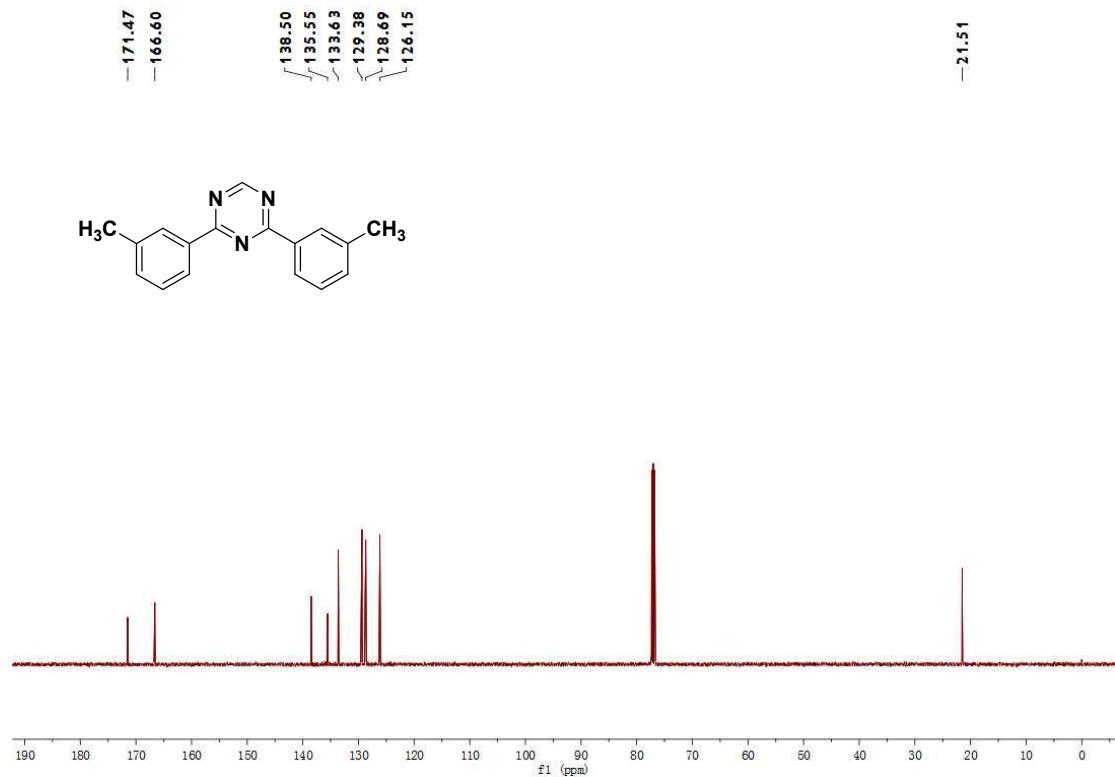
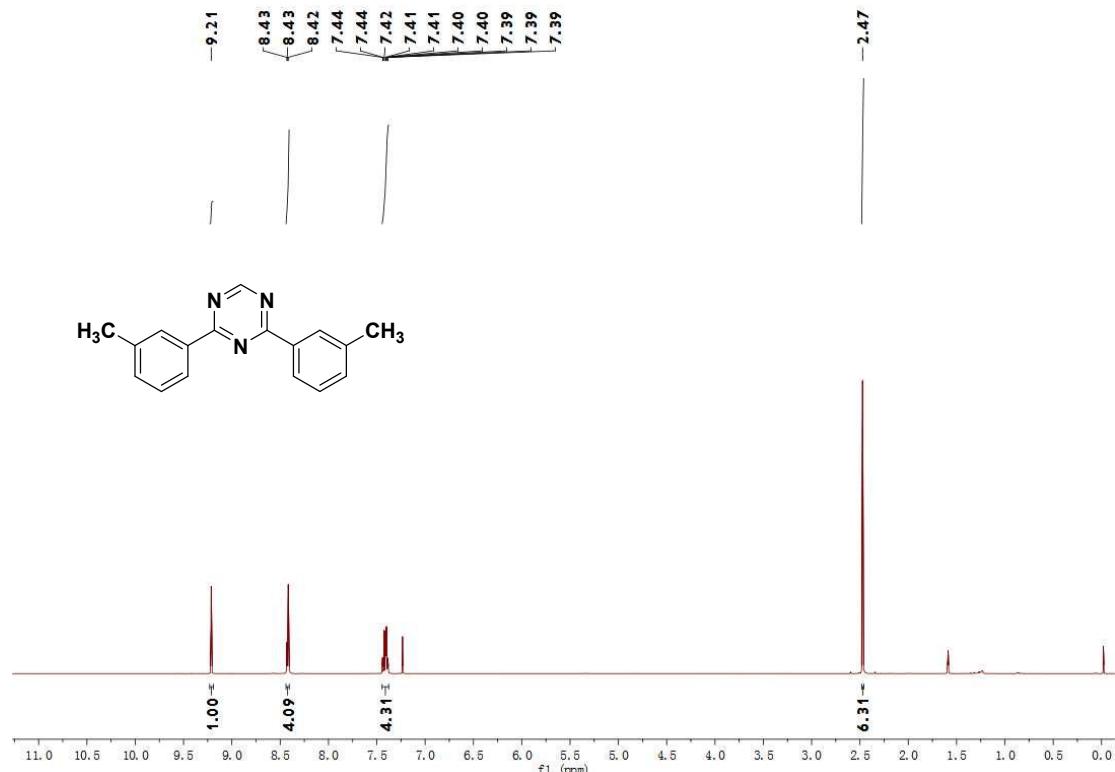
**2,4-bis(4-nitrophenyl)-1,3,5-triazine (3g)**



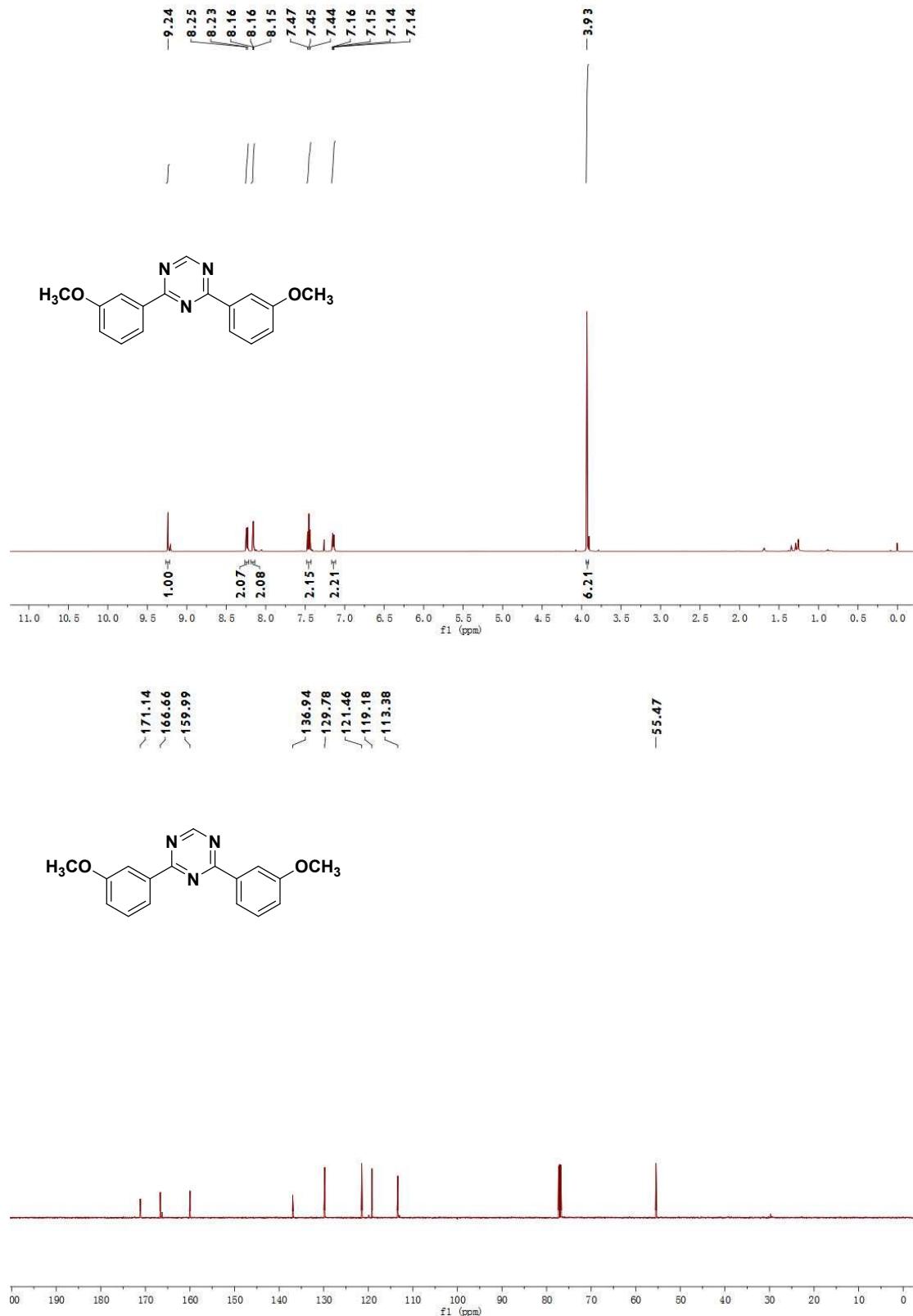
**2,4-bis(4-(trifluoromethyl)phenyl)-1,3,5-triazine (3h)**



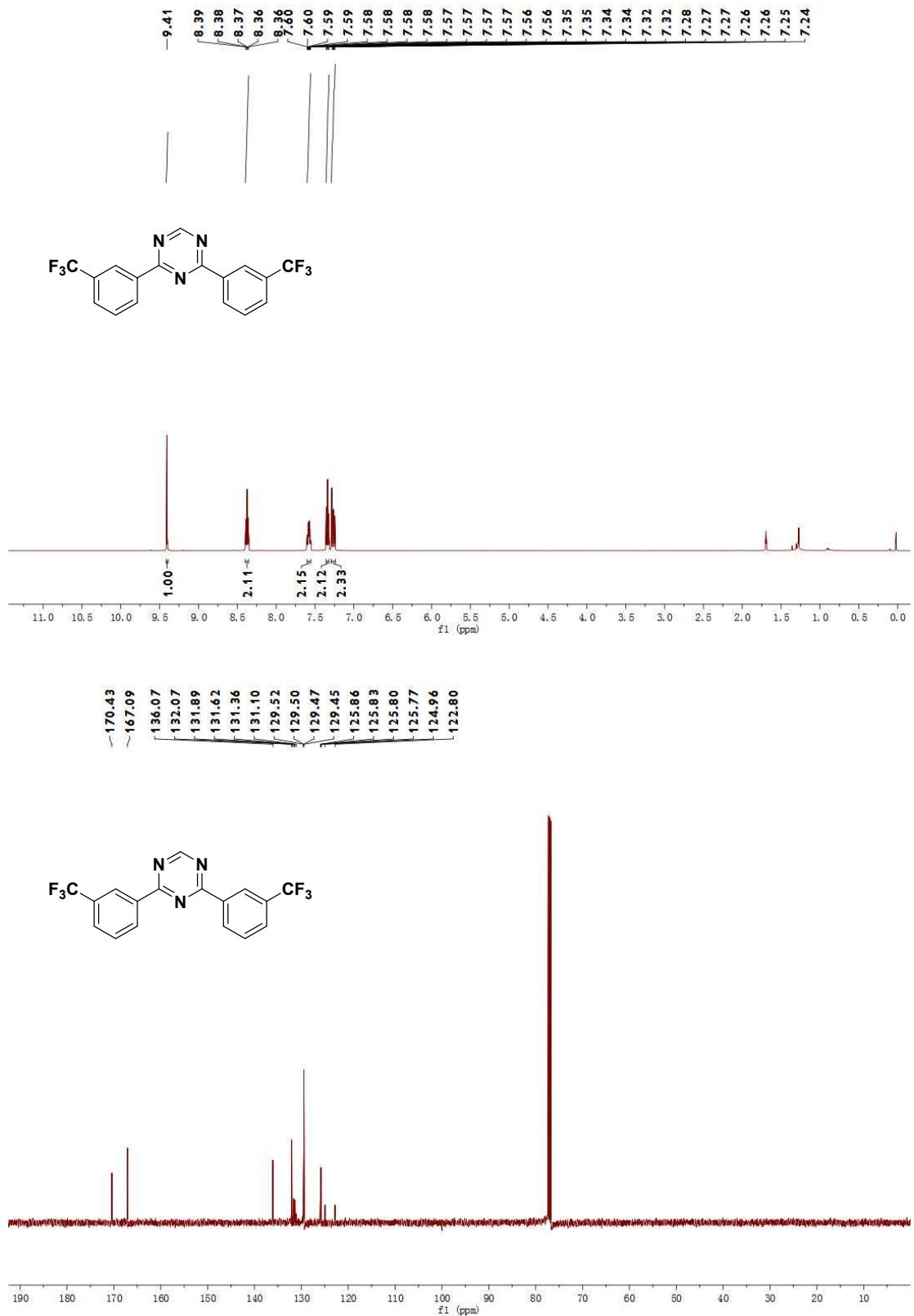
**2,4-di-m-tolyl-1,3,5-triazine(3i)**



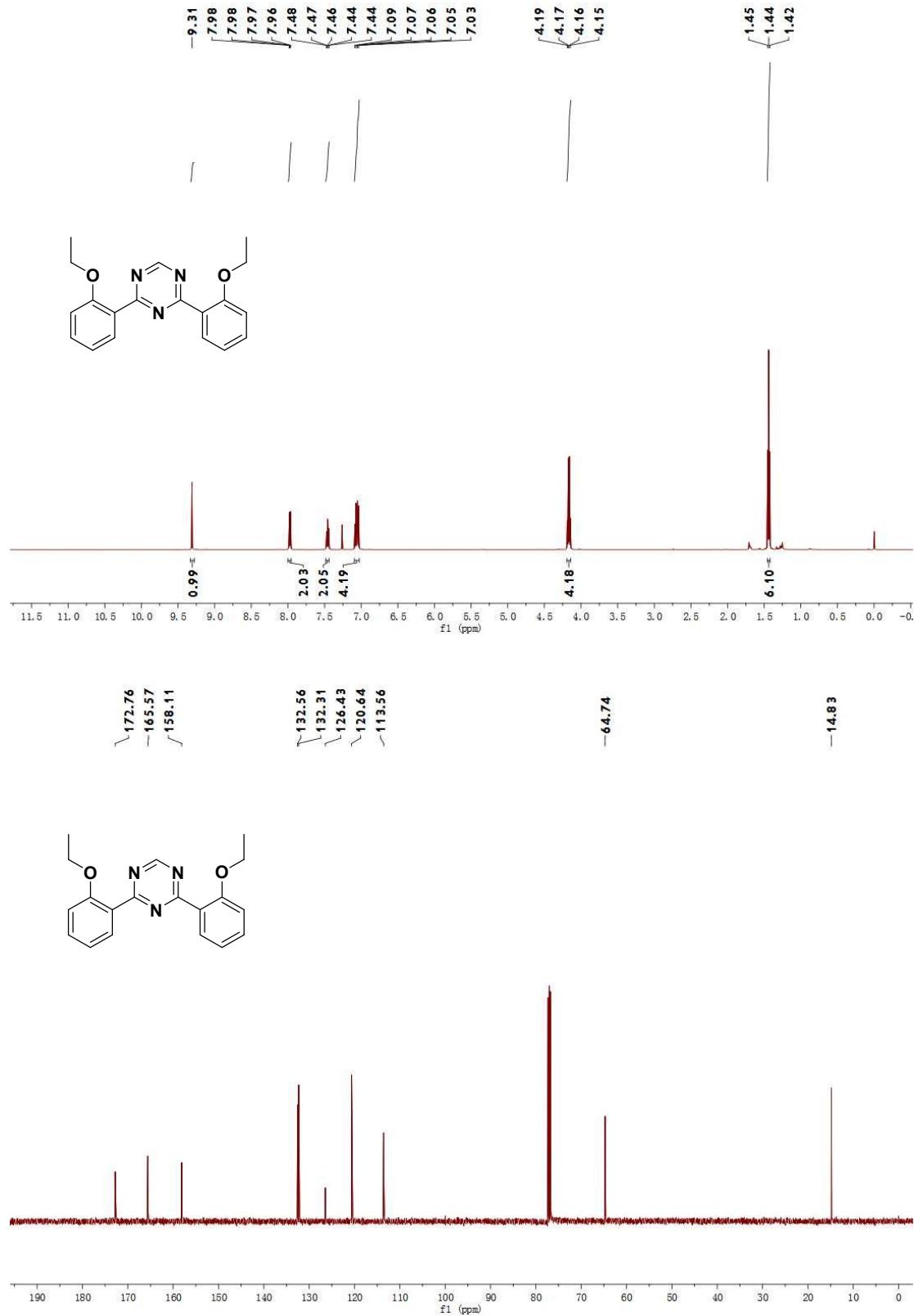
**2,4-bis(3-methoxyphenyl)-1,3,5-triazine (3j)**



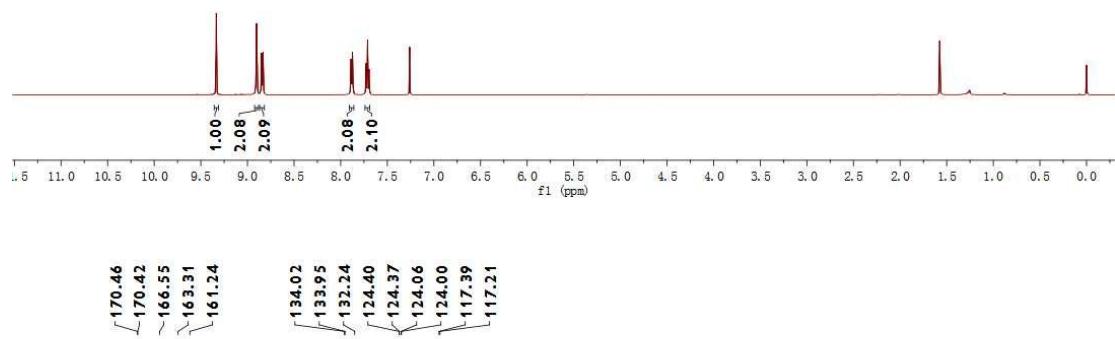
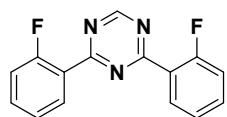
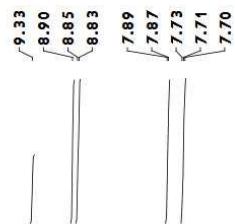
### 2,4-bis(4-(trifluoromethyl)phenyl)-1,3,5-triazine (3k)



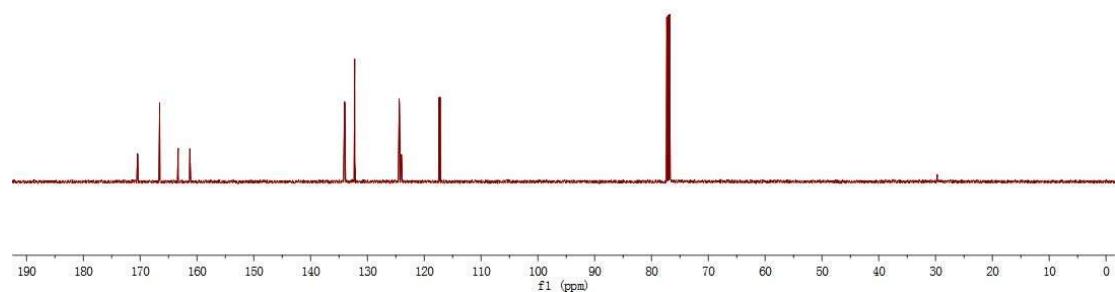
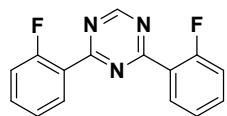
**2,4-bis(2-ethoxyphenyl)-1,3,5-triazine (3l)**



**2,4-bis(2-fluorophenyl)-1,3,5-triazine (3m)**

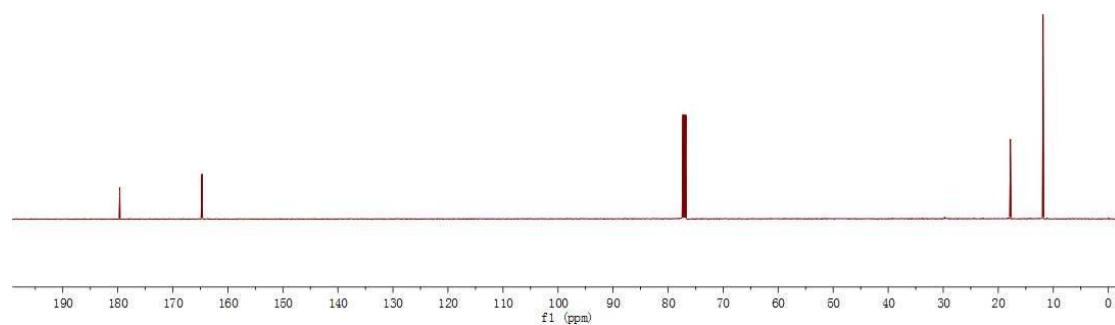
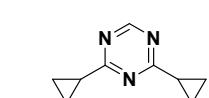
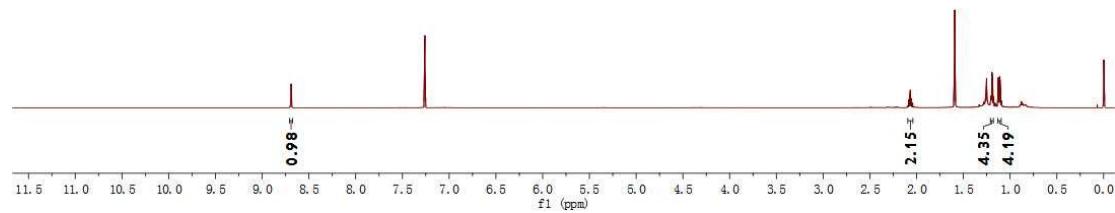
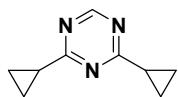


170.46  
170.42  
~166.55  
163.31  
161.24  
134.02  
133.95  
132.24  
124.40  
124.37  
124.06  
124.00  
117.39  
117.21

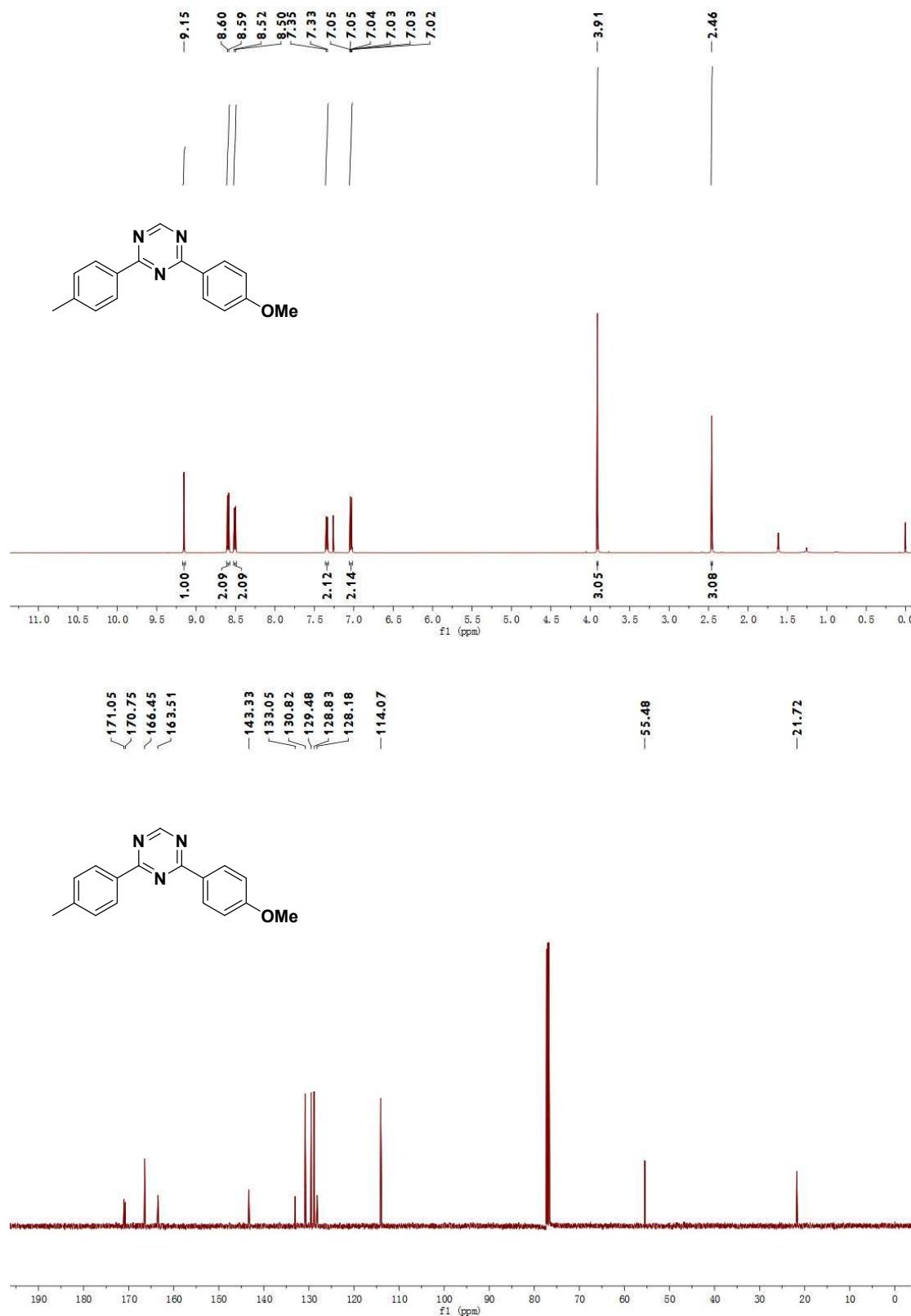


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

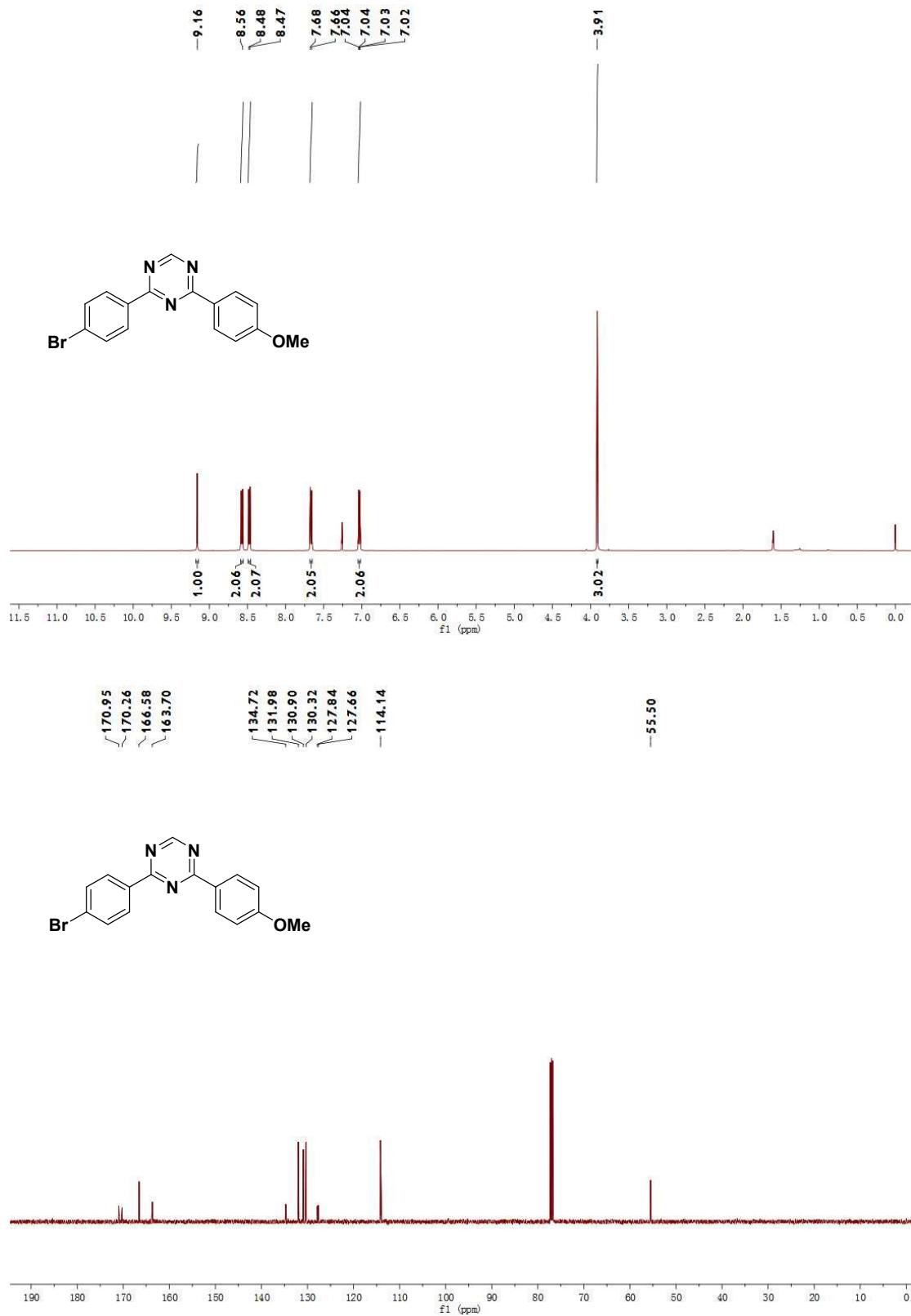
### **2,4-dicyclopropyl-1,3,5-triazine (3n)**



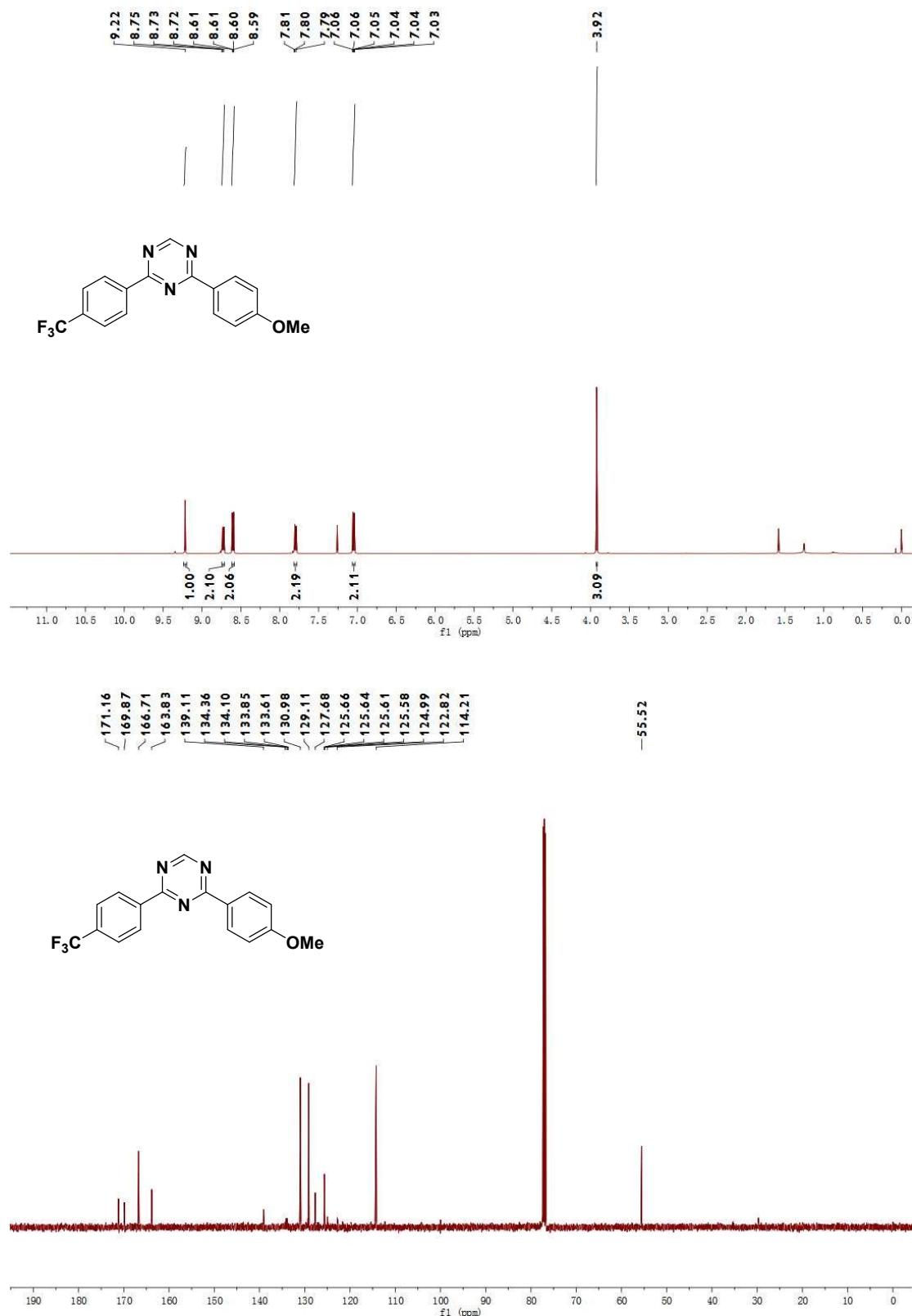
**2-(4-methoxyphenyl)-4-(p-tolyl)-1,3,5-triazine (3bc)**



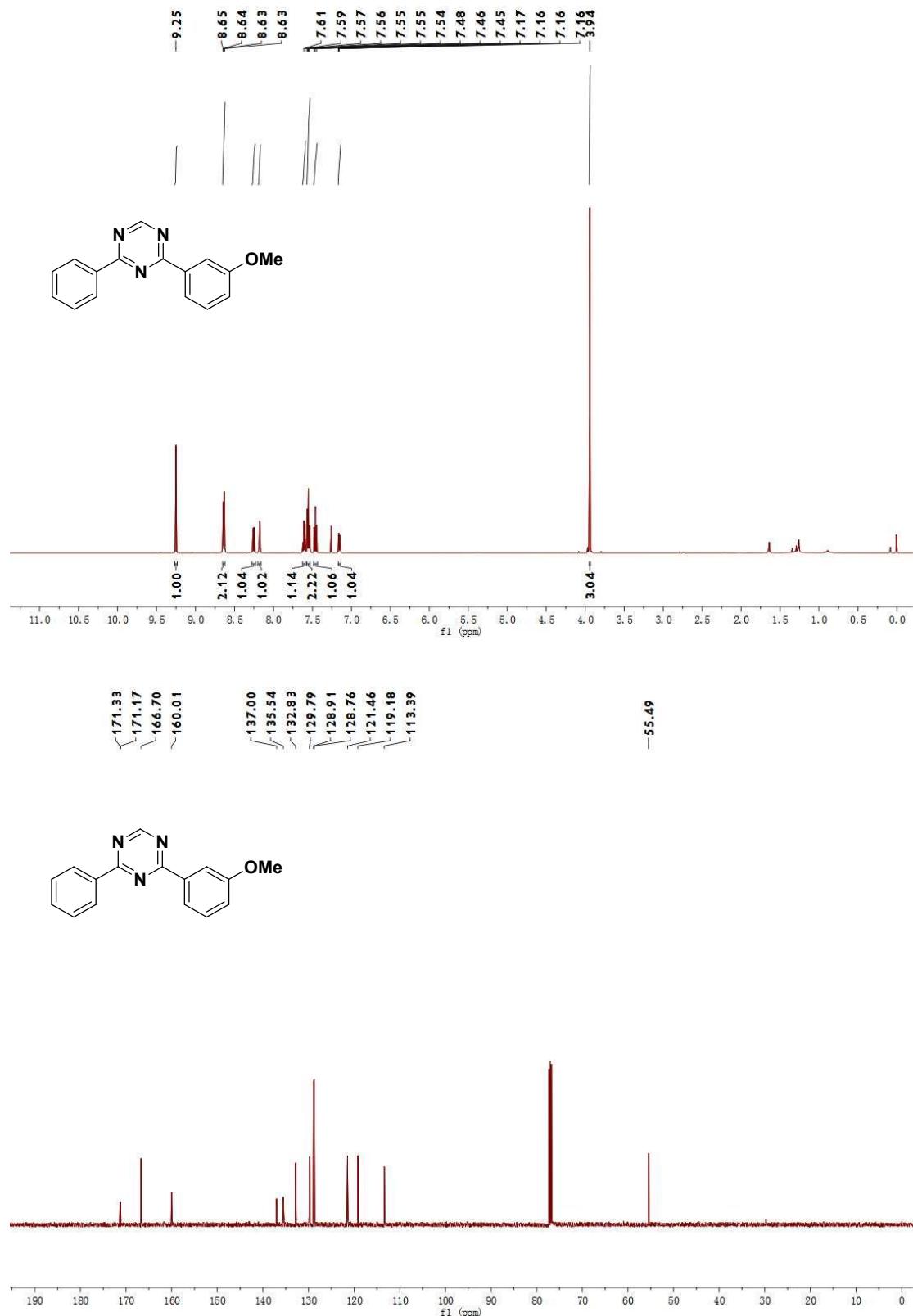
**2-(4-bromophenyl)-4-(4-methoxyphenyl)-1,3,5-triazine (3cf)**



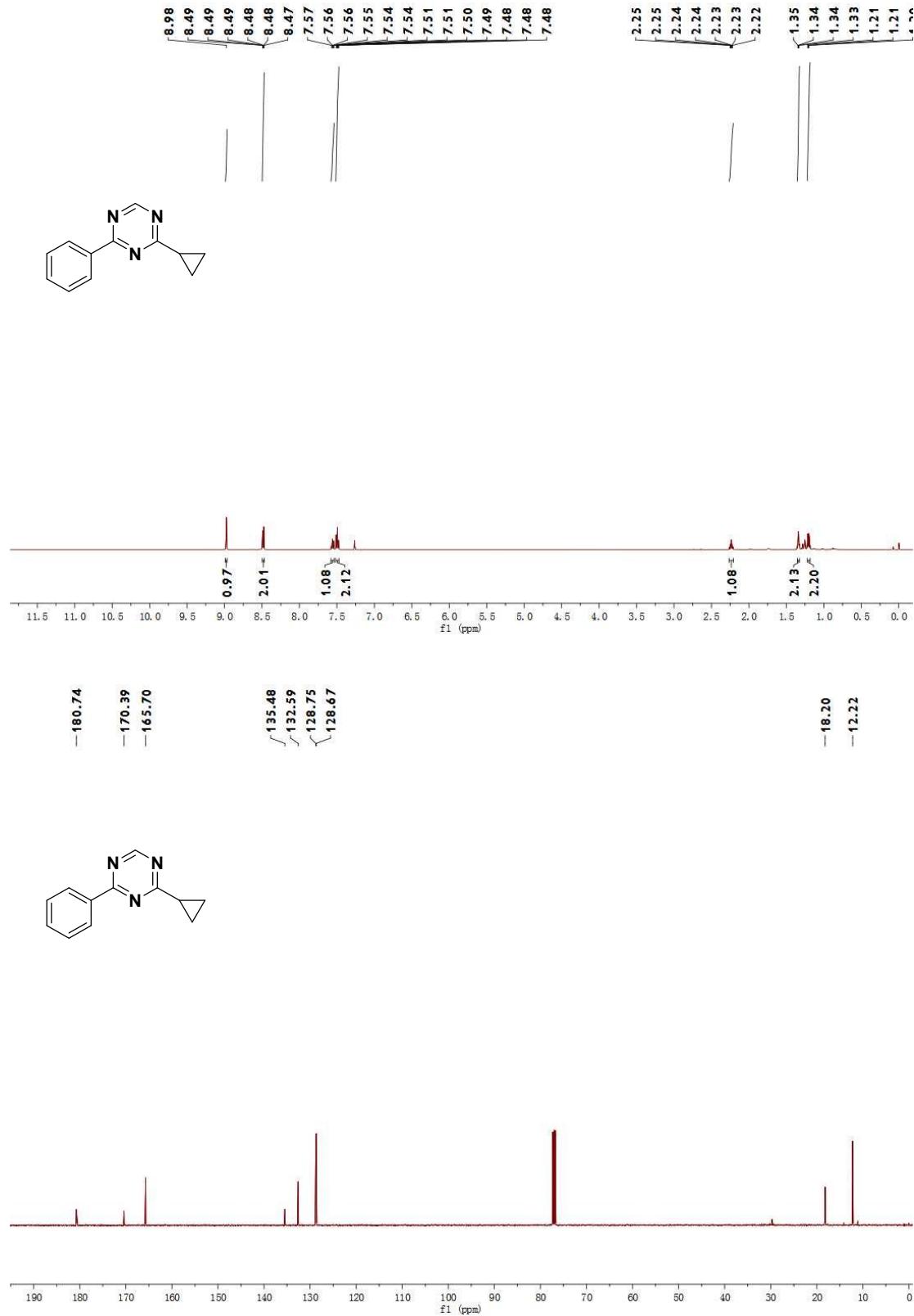
**2-(4-methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-1,3,5-triazine (3cg)**



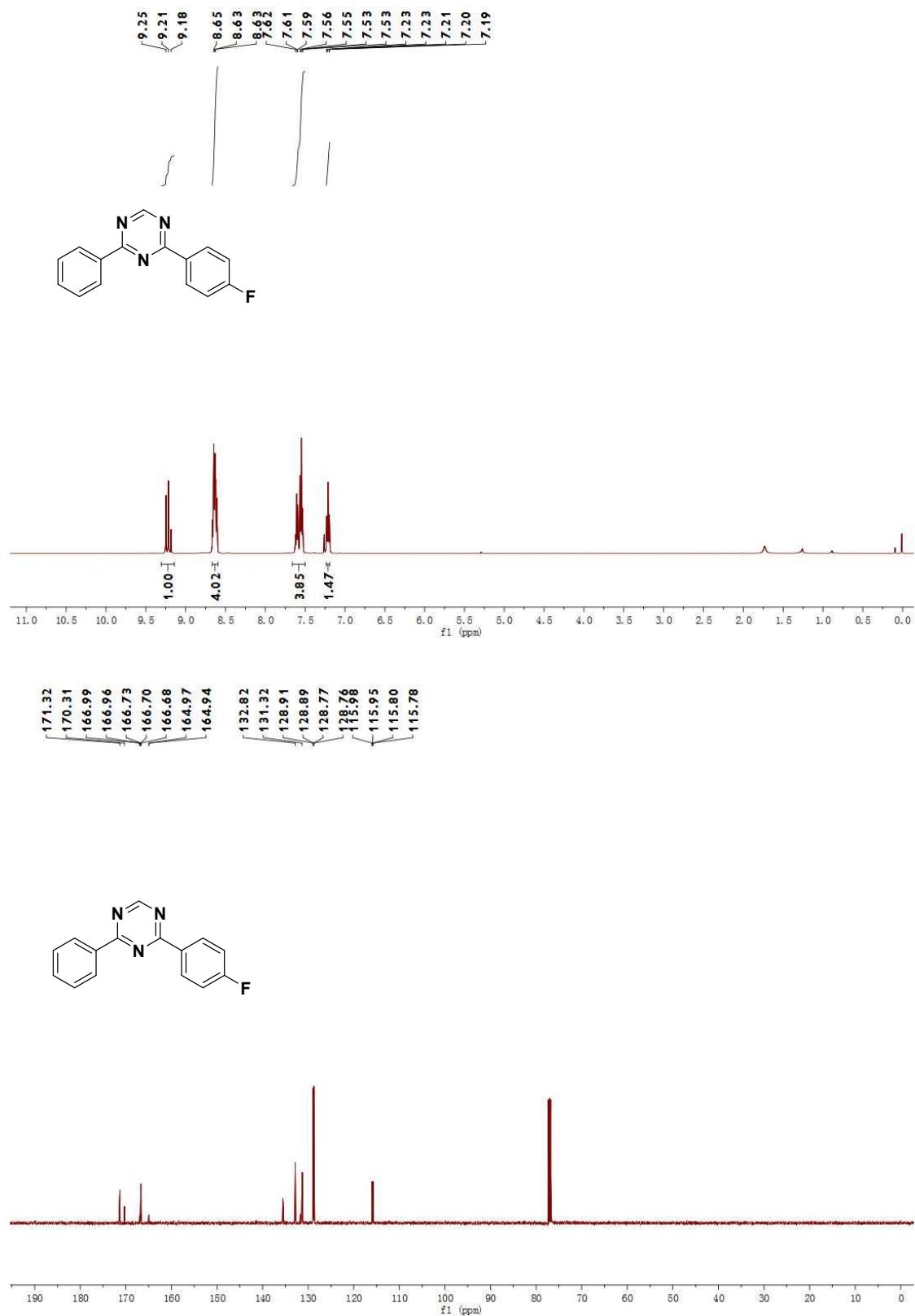
**2-(3-methoxyphenyl)-4-phenyl-1,3,5-triazine (3aj)**



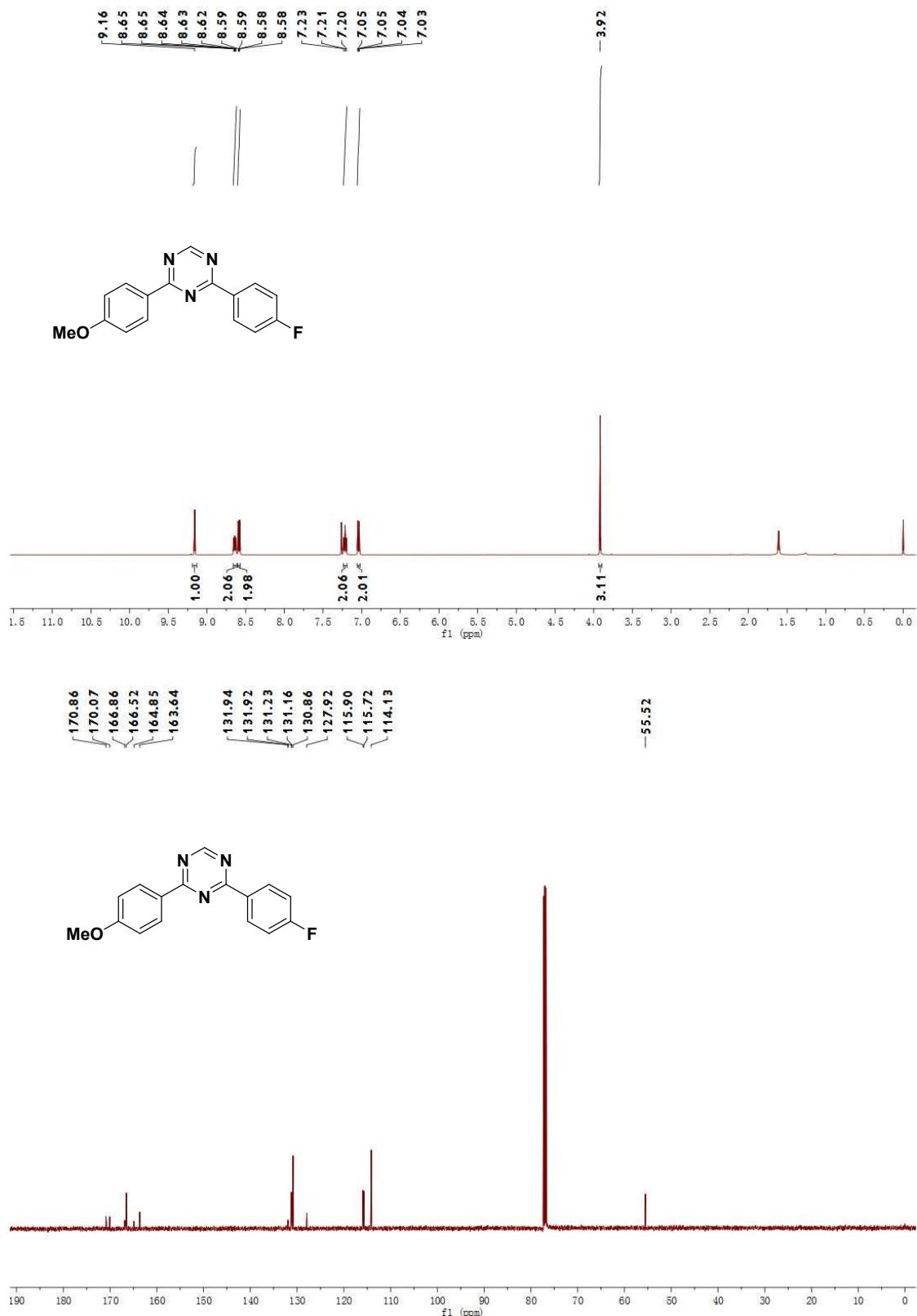
**2-cyclopropyl-4-phenyl-1,3,5-triazine (3an)**



**2-(4-fluorophenyl)-4-phenyl-1,3,5-triazine (3ad)**



**2-(4-fluorophenyl)-4-(4-methoxyphenyl)-1,3,5-triazine (3dc)**



**2-cyclopropyl-4-(4-fluorophenyl)-1,3,5-triazine (3dn)**

